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SYNTHESIS AND CRYSTAL AND MOLECULAR STRUCTURE OF  
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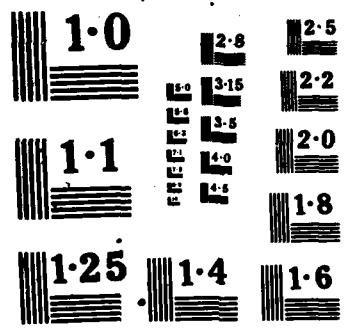
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The new compound $\text{In}(\text{C}_5\text{Me}_5)_3$ has been prepared and characterized by an X-ray structural study as an octahedral cluster. This new indium(I) compound is a golden yellow, volatile crystalline solid at room temperature. An X-ray structural study demonstrates that the compound crystallizes in the rhombohedral space group $R\bar{3}$ ( $\text{C}_{2h}$ ; No. 148) with unit cell parameters (hexagonal setting) $a=20.182(4)$ , $c=13.436(3)\text{\AA}$ , $V=4739(2)\text{\AA}^3$ and $Z=18$ . The structure refined to $R_F=3.6\%$ and $R_{wF}=3.3\%$ for all 1870 unique data. The crystal consists of an		

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20. octahedral cluster  $[\text{In}(\text{C}_5\text{Me}_5)]_6$  with indium atoms on the interior and  $\eta^5\text{-C}_5\text{Me}_5$  units on the exterior. All pentamethylcyclopentadienyl rings exhibit  $\eta^5$ -coordination to indium but the "centroid"  $\rightarrow$  indium vectors do not point toward the center of the hexaindium cluster as in other main-group clusters.

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TECHNICAL REPORT NO. 15

Synthesis and Crystal and Molecular Structure of

$\text{In}(\text{C}_5\text{Me}_5)_3$ -An Apparent Octahedral Cluster

by

O.T. Beachley, Jr.<sup>\*</sup>, Melvyn Rowen Churchill, James C. Fettingner,

J.C. Pazik, and L. Victoriano

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(Contribution from the Department of Chemistry, State University of New York  
at Buffalo, Buffalo, N.Y. 14214)

SYNTHESIS AND CRYSTAL AND MOLECULAR STRUCTURE OF  
 $\text{In}(\text{C}_5\text{Me}_5)$ -AN APPARENT OCTAHEDRAL CLUSTER

by

O.T. Beachley, Jr.<sup>\*</sup>, Melvyn Rowen Churchill, James C. Fettingier,  
J.C. Pazik, and L. Victoriano

ABSTRACT

*(C subscript 5 Me subscript 5) Sub 3 i Cubic Anaginal*

The new compound  $\text{In}(\text{C}_5\text{Me}_5)$  has been prepared and characterized by an X-ray structural study as an octahedral cluster. This new indium(I) compound is a golden yellow, volatile crystalline solid at room temperature. An X-ray structural study demonstrates that the compound crystallizes in the rhombohedral space group  $R\bar{3}$  ( $C_{3i}^2$ ; No. 148) with unit cell parameters (hexagonal setting)  $a=20.182(4)$ ,  $c=13.436(3)\text{\AA}$ ,  $V=4739(2)\text{\AA}^3$  and  $Z=18$ . The structure refined to  $R_F=3.6\%$  and  $R_{WF}=3.3\%$  for all 1870 unique data. The crystal consists of an octahedral cluster  $[\text{In}(\text{C}_5\text{Me}_5)]_6$  with indium atoms on the interior and  $\eta^5\text{-C}_5\text{Me}_5$  units on the exterior. All pentamethylcyclopentadienyl rings exhibit  $\eta^5$ -coordination to indium but the "centroid"  $\rightarrow$  indium vectors do not point toward the center of the hexaindium cluster as in other main-group clusters.

(Contribution from the Department of Chemistry, State University of New York  
at Buffalo, Buffalo, N.Y. 14214)

SYNTHESIS AND CRYSTAL AND MOLECULAR STRUCTURE OF  
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The synthesis and structural characterization of group 13 compounds can play an important role in the development of main-group organometallic chemistry. A topic of current interest centers on compounds with the metal in positive oxidation states which are less than three. In group 13 chemistry the fully characterized compounds in the +1 oxidation state include  $\text{In}(\text{C}_5\text{H}_5)^{1,2}$  and  $\text{Tl}(\text{C}_5\text{H}_5)^3$ . The indium(I) compound is most readily prepared from  $\text{InCl}$  and  $\text{LiC}_5\text{H}_5$  in diethyl ether<sup>2</sup>. An X-ray structural study<sup>4</sup> reveals the presence of zig-zag polymeric chains of  $\text{In}(\eta^5\text{-C}_5\text{H}_5)$  units with very long  $\text{In} \cdots$  "centroid" distances ( $3.19\text{\AA}$ ). The distance between indium atoms which are arranged in apparent triangles is  $3.99\text{\AA}$ . In contrast, the gas phase<sup>5</sup> consists of discrete monomeric  $\text{In}(\eta^5\text{-C}_5\text{H}_5)$  units with  $\text{In}-\text{C}$  distances ( $2.621\text{\AA}$ ) which are significantly shorter than that observed for

the solid state. In order to understand more fully the nature of organoindium(I) compounds, we report the synthesis and crystal and molecular structure of  $\text{In}(\text{C}_5\text{Me}_5)$ . The new compound  $\text{In}(\text{C}_5\text{Me}_5)$  was prepared from  $\text{InCl}$  (4.92 mmol) and  $\text{Li}(\text{C}_5\text{Me}_5)$  (5.00 mmol) in diethyl ether. This combination of reagents leads to the formation of a deep yellow solution and heavy grey precipitate, indicative of a mixture of  $\text{LiCl}$  and indium metal. The yellow solution was separated from the solid in the reaction mixture by filtration. Removal of solvent and subsequent sublimation of the resulting yellow solid at  $55^\circ\text{C}$  and 0.001 torr led to the isolation of  $\text{In}(\text{C}_5\text{Me}_5)$  as a yellow orange crystalline solid<sup>7</sup> (0.710g, 2.84 mmol, 57.7% yield based on  $\text{InCl}$ ). Crystals of crystallographic quality were grown by sublimation at  $55^\circ\text{C}$  under high vacuum. The compound is exceedingly air and moisture sensitive. An initial product of hydrolysis is indium metal. Trace amounts of moisture convert the yellow orange crystals to a dark grey-green solid.

$\text{In}(\text{C}_5\text{Me}_5)$  crystallizes in the rhombohedral space group  $R\bar{3}$  ( $C_{3i}^2$ ; No. 148) with unit cell parameters (hexagonal setting)  $a=20.182(4)$ ,  $c=13.436(3)\text{\AA}$ ,  $V=4739(2)\text{\AA}^3$  and  $Z=18$ . X-ray diffraction data (Mo K $\alpha$ ,  $2\theta=4.5-50.0^\circ$ ) were collected on a Syntex P2<sub>1</sub> automated four-circle diffractometer using the coupled  $\theta$ - $2\theta$  scan technique and were corrected for the effects of absorption ( $\mu=21.7\text{ cm}^{-1}$ ). The structure was solved by Patterson and difference-Fourier methods and refined to  $R_F=3.6\%$  and  $R_{WF}=3.3\%$  for all 1870 unique data ( $R_F=2.5\%$  and  $R_{WF}=2.9\%$  for those 1444 reflections with  $|F_o|>6\sigma(|F_o|)$ ).

The packing of  $\text{In}(\text{C}_5\text{Me}_5)$  units within the unit cell is illustrated in Figure 1. They are arranged about centers of  $\bar{3}$  ( $S_6$ ) symmetry with indium atoms on the interior and  $\eta^5\text{-C}_5\text{Me}_5$  units on the exterior of hexameric units. The In-In distances are all chemically equivalent, with values of  $3.963(1)\text{\AA}$  around the  $C_3$  axis and  $3.942(1)\text{\AA}$  between atoms in the two triangular units;



the molecule is thus based upon an octahedral  $\text{In}_6$  core (see Figure 2). This In-In distance<sup>4</sup> is very similar to that observed in  $\text{In}(\text{C}_5\text{H}_5)$ .

Individual In-C distances range from 2.581(4) through 2.613(4) Å, averaging 2.595 Å, and the In-"centroid" distance is 2.302 Å. Carbon-carbon distances within the carbocyclic ring are 1.397(6)-1.417(6) Å (average = 1.409 Å), while C(ring)-Me distances are 1.496(10)-1.515(9) Å (average = 1.508 Å). The  $\text{C}_5\text{Me}_5$  skeleton has  $\text{C}_{5v}$  symmetry with all Me groups displaced from the ring and away from the indium atom by 0.092(8)-0.110(7) Å; the average deviation of 0.101 Å corresponds to a perpendicular angular displacement of 3.84°.

The volatility of  $\text{In}(\text{C}_5\text{Me}_5)$  suggests that the octahedral cluster has only marginal stability. Monomeric species are probably formed in the gas phase. However, some type of bonding interactions is required to counteract the repulsions between the ends of the dipole moments associated with bringing six monomeric pentamethylcyclopentadienylindium units together in the solid state. Cyclopentadienylindium(I) has a significant experimental dipole moment<sup>8</sup> of 2.2D with the indium atom and its associated lone pair being the negative end of the molecule. It is also of interest that the structure of the hexaindium cluster  $\text{In}_6(\text{C}_5\text{Me}_5)_6$  is significantly different from that observed for other stable main-group element clusters such as those for boron hydrides<sup>9,10,11</sup> and boron subhalides<sup>12,13</sup>. All boron containing clusters have boron-->hydrogen and boron-->halogen vectors which point toward the centers of the clusters. The indium<--centroid vectors do not point toward the center. The only fully characterized octahedral boron cluster<sup>14</sup> is  $\text{B}_6\text{H}_6^{2-}$ . The boron subhalide  $\text{B}_6\text{Br}_6$  has been observed but the compound has not been fully characterized<sup>13</sup>. Similarly,  $\text{B}_6[\text{NMe}_2\text{AlMe}_2]_6$  has been reported but no structural data are available<sup>15</sup>. Orbital and skeletal

electron counting conventions by Wade<sup>9</sup> and Williams<sup>10</sup> require each skeletal atom to provide one sp hybrid orbital and two p atomic orbitals for cluster bonding. Thus, the octahedral boron cluster,  $B_6H_6^{2-}$ , has seven pairs of skeletal bonding electrons whereas  $In_6(C_5Me_5)_6$  has only six apparent electron pairs. The resulting disparities between the structural characteristics and the thermodynamic stabilities of these octahedral clusters could originate with the atomic orbitals which each skeletal atom provides for cluster bonding and/or with the number of available skeletal bonding electrons. Further details of the chemistry of pentamethylcyclopentadienyl- and related cyclopentadienyl-indium(I) derivatives will be reported in the near future.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths and bond angles (    pages). Ordering information is given on any current masthead page.

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CAPTIONS TO FIGURES.

Figure 1. A stereoscopic view, showing the packing of the  $\text{In}(\eta^5\text{-C}_5\text{Me}_5)$  units into octahedral clusters (ORTEP-II diagram, 30% probability ellipsoids for all non-hydrogen atoms).

Figure 2. A view of the hexameric octahedral cluster.

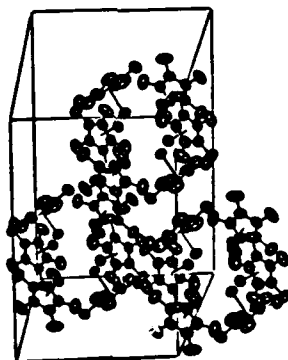
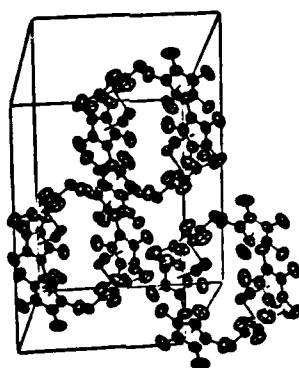


Figure 1.

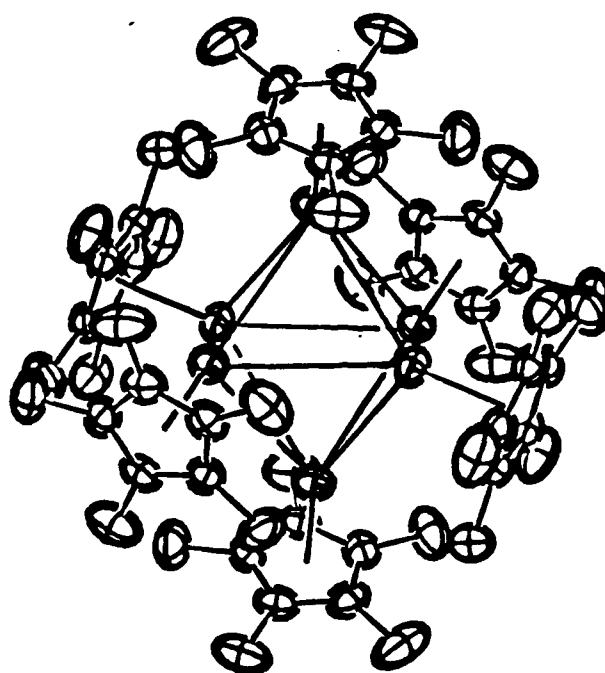


Figure 2.

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